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Description of EP0230977

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Defoamer on base of oil in water emulsions

From the DE-PS 21 57 033 is a method to the defoaming of aqueous systems by means of emulsions known, the C12 to C22-Alkanole and/or C12 to C22-Fettsäureester two or trivalent alcohols, as well as paraffinic oil and/or C12 to C22-Fettsäuren as defoamer as well as actual known additives of interface-active materials as emulsifying agents contained. The emulsified water-insoluble materials have a middle particle size from 4 to 9 μ m. The known antifoaming agent emulsions have the disadvantage that they up-frame with the storage and thicken partially even so strongly that such mixtures then no longer pumped to become to be able.

From the US-PS 34 08 306 a method is to the defoaming of aqueous systems known, with which one uses an antifoaming agent mixture, those from 80 to 97 Gew. - % of a water-soluble hydrophoben organic fluid (e.g. Mineral oil, langkettige alcohols, esters or amines) and from 3 to 20 Gew. - % hydrophobierten finely divided solids (e.g. Silicic acid, bentonite, talc or titania) exist. The antifoaming agent mixture can if necessary up to 5 Gew. - % of an surface-active agent contained. A substantial feature of these antifoaming agent mixtures consists of the fact that the finely divided solids with materials are hydrophobiert (e.g. Dimethylpolysiloxanölen), which are usually used as defoamers. The production of hydrophobierter finely divided solids is technically expensive.

From the EP-application 149,812 is known, defoamer on base of oil in water emulsions, with those the oil phase of the emulsion

(A) a C12 to C26-Alkohol, distillation residues, those with the production of alcohols with a higher carbon number by Oxosynthese or after the Ziegler method obtained if necessary and still alkoxyliert are and/or
(B) a fatty acid ester from C12 to C22-Carbonsäuren with an in to trivalent c1 to C18-Alkohol and if necessary
(C) an hydrocarbon with a boiling point above 200 DEG C or fatty acids with 12 to 22 carbon atoms
contains, to 15 to 60 Gew. - % at the structure of the emulsion involved is and a middle particle size of 0,5 to 15 μ m has, by additive of 0,5 to 5 Gew. - % of an high molecular, water-soluble Homo or copolymer of acrylic acid, methacrylic acid, to stabilize acrylamide or methacrylamide against viscosity increase and Aufrahmen with the bearing journal.

The invention is the basis the object, the known defoamers under larger and/or. to arrange more pollution free complete preservation of the effectiveness, i.e. to reduce the chemical Sauerstoffbedarf in effluents.

The object becomes inventive dissolved by defoamers on base of oil in water emulsions, with those the oil phase of the emulsions

(A) a C12 to C26-Alkohol, distillation residues, those with the production of alcohols with a higher carbon number by Oxosynthese or after the Ziegler method available and those if necessary. still alkoxyliert is and/or
(B) a fatty acid ester from C12 to C22-Carbonsäuren with an in to trivalent c1 to C18-Alkohol and if necessary
(C) an hydrocarbon with a boiling point above 200 DEG C or fatty acids with 12 to 22 carbon atoms
contains, to 5 to 50 Gew. - % at the structure of the emulsion involved is and a middle particle size of < 25 μ m has, if the oil in water emulsions superficially did not hydrophobierte, finely divided, practically water-insoluble inert solids contains.

The component (A) of the oil in water emulsions consists particularly of natural or synthetic alcohols with 12 to 26 carbon atoms or alcohol mixtures. Examples are Myristylalkohol, cetyl alcohol and stearyl alcohol. The synthetic alcohols, which are for example available after the Ziegler method by oxidation of aluminium alkyls, are satisfied, straight-chain, normal Alkohole. Synthetic alcohols become also obtained by Oxosynthese. Here it usually concerns alcohol mixtures. When component know (A) of the oil phase of the antifoaming agent emulsions in addition distillation residues, which become with the production that alcohols managing specified by Oxosynthese or after the Ziegler method obtained, are used. As component (A) of the oil phase of the antifoaming agent emulsions are suitable also alkoxyliert distillation residues, which are producible after the Ziegler method with the above-mentioned method to the production of higher alcohols by Oxosynthese or. Man erhält die oxalkylierten Destillationsrückstände dadurch, dass man die obengenannten Destillationsrückstände mit Ethylenoxid oder mit Propylenoxid oder auch mit einer Mischung aus Ethylenoxid und Propylenoxid umgesetzt. Per OH-group of the alcohol in the distillation residue become up to 5 ethylenoxid and/or. Groups of propylene oxides of attached. Preferably added one per OH-group of the alcohol in the distillation residue 1 to 2 groups of ethyl oxides.

As component (B) of the oil phase of the antifoaming agent emulsion one uses fatty acid esters from C12 to C22-Carbonsäuren with an in to trivalent c1 to C18-Alkohol. The fatty acids, which are the basis the esters, are for example Laurylsäure, Myristinsäure, palmitic acid, stearic acid, Arachinsäure and behenic acid. Preferably one uses palmitic acid

or stearic acid esters. One can use univalent c1 to C18-Alkohole for the esterification of the carboxylic acids mentioned, e.g. Methanol, Ethanol, Propanol, Butanol, Hexanol, Decanol und Stearylalkohol als auch zweiwertige Alkohole, wie Ethylenglykol oder dreiwertige Alkohole wie Glycerin. The multi-valued alcohols can be completely or partial third. The oil phase of the antifoaming agent emulsions contains a compound of the component (A) or (B) also of the mixtures from the components (A) and (B).

The components (A) and (B) can be used in any ratio to the production of the defoamers. In the practice for example mixtures from (A) and (B) preserved, the 40 to 60 % (A) and 60 to 40 Gew. - % (B) contained.

The oil phase of the emulsion can become additionally still by a further class water-insoluble compounds formed, which becomes in the following as component (C) referred. The compounds of the component (C) can up to 50 Gew. - %, related to the components (A) and (B) at the structure of the oil phase of the antifoaming agent emulsions involved its. They can be added either to a mixture from the components (A) and (B) or everyone of the compounds specified under (A) or (B). As component (C) hydrocarbons with a boiling point are suitable with 1013 mbar of more than 200 DEG C and a setting point under 0 DEG C or fatty acids with 12 to 22 carbon atoms. Preferably paraffinic oils are suitable as hydrocarbons, as the paraffin mixtures usual in the commerce, which become also referred as Weissöl.

Those compounds managing specified (A) and/or (B) as well as (C) form the oil phase of the oil in water emulsions if necessary. The oil phase is to 5 to 50 Gew. - % at the structure of the oil in water emulsion involved, during the portion the aqueous phase at the structure of the oil in water emulsions 95 to 50 Gew. - amounts to %, whereby the weight percentage adds itself in each case to 100. The middle particle size of the oil phase of the oil in water emulsion is appropriate below 25 μm and amounts to preferably 0, 5 to 15 μm .

The substantial feature of the present invention consists of it that the oil phase of the oil in water emulsions did not hydrophobisierte superficially, finely divided, practically water-insoluble inert solids contains. The particle diameter of the finely divided, practically water-insoluble inert solids is appropriate below 20 μm , preferably in the range of 0, 1 to 10 μm . Die erfindungsgemässen Entschäumer können auch dadurch hergestellt werden, dass man die feinteiligen inerten Feststoffe in einen bekannten Öl-in-Wasser-Entschäumer einemulgiert, z.B. into an emulsion of the compounds (A) and/or (B) and if necessary (C) in waters. For the inventive defoamers one can use all inert solids, which do not react with the components of the antifoaming agent mixture and which in water insoluble are also practical. Preferably one uses kaolin, chalk, calcium sulfate, barium sulphate, talcum powder, micro-crystalline cellulose and/or crosslinked starch as inert solids. Concerning the applicability of solids it exist - apart from the fact that the solids inert are not to be hydrophobisiert and - no Einschränkungen. Man can both inorganic and organic superficially untreated solids use, e.g. are suitable except the solids specified already the subsequent: Layer silicates, like bentonite, Montmorillonit, Nontronit, Hectorit, Saponit, Volkonskoit, Sauconit, Beidellit, Allevaridit, Illit, Halloysit, attapulgite and Sepiolit as well as titania, alumina, silicon oxide, Satinweiss, synthetic aluminium silicates, crosslinked urea formaldehyde and Melamin formaldehyde or - isobutyraldehyd condensates as well as Homo and copolymers of the styrene, which are for example from the GB-PS 1,229 503 known. Urea formaldehyde condensates, which become also referred as ureaurea urea, one receives by condensing from Vorkondensaten from urea and formaldehyde in the molar ratio from 1 or less than 1 in presence of strongly acid catalysts at pH values below 2 (vgl. de AS 2 110 309) or after the method of the US-PS 3,931 063. In addition in accordance with the DE-OS 25 47 966 comes available condensation products into considerations. One knows mixtures of the inorganic inert solids, which organic inert solids as well as mixtures from inorganic and organic inert solids begin. The organic and inorganic finely divided solids are used in not hydrophobierter form and to require therefore no previous coating layer and/or. Treatment with hydrophobierenden materials.

The solids become preferably used in a quantity that 5 to 30 % of the oil phase of the oil in water emulsions is replaced by them.

The production of the inventive defoamers made preferably so that one if necessary emulsifies first the finely divided inert solids with the compounds (A) and/or (B) and (C) homogenized and thereby the resultant mixture subsequent in waters. The inventive defoamers can become also thereby prepared that one in-emulsifies the finely divided inert solids into a known oil in water defoamer, e.g. into an emulsion of the compounds (A) and/or (B) and if necessary (C) in waters. If the organic compounds, which form the oil phase, represent solid fabrics at ambient temperature, they are first melted. One registers then into the melt one or more finely divided inert solids, whereby one provides for a good mixing of the components. Mixing the components (A) until (C) with the inert solids knows with temperatures from 50 to 100 DEG C are made. With it the resultant mixture then to the production of the oil in water emulsions in waters one emulsifies. For this one uses the interface-active fabrics usually coming into considerations, who have a HLB value of more than 6. It concerns with these interface-active materials oil in water emulsifying agents and/or. around typical wetting agents. From the interface-active fabrics one can use anionic, cationic or nichtionische compounds. Preferred ones become anionic or nichtionische and/or. Mixtures from anionic and nichtionischen interface-active materials used. Materials of the mentioned type are for example sodium or ammonium salts of higher fatty acids, how ammonium oleate or - stearat, oxalkylierte alkyl phenols, as Nonylphenol or Isooctylphenol, which are converted in the molar ratio 1:2 to 50 with ethylene oxide, oxethylierte insatiated oils, e.g. the reaction products of 1 mol of castor oils and 30 to 40 mol ethylene oxide or the reaction products from 1 mol of Spermylalkohol with 60 to 80 mol ethylene oxide. As emulsifying agents becomes also preferably sulfierte Oxethylierungsprodukte of Nonylphenol or Octylphenol used, which are present as sodium or ammonium salt of the corresponding sulfuric acid half esters. 100 Gew. - Parts of the oil in water emulsions contained usually 0, 5 to 5 Gew. - Parts of an emulsifying agent or an emulsifying agent mixture. The main quantity of the emulsifying agent is in the aqueous phase dissolved. Except the emulsifying agents specified already one can still protective colloids, like high molecular polysaccharides and soaps or other usual additives, like stabilisers, see. EP-application 149,812, use. The a emulsifying of the oil phase (mixture from the components (A) to (C) and the inert solids) can using commercial apparatuses, e.g. Dispergators, take place. If the oil phase should be present as solid mass, it is first melted and in-emulsified then in waters. The a emulsifying of the oil phase in waters can take place at ambient temperature as well as with higher temperatures, e.g. in the temperature range from 50 to 95 DEG C.

The antifoaming agent emulsions have immediately after the production a viscosity in the range from 300 to 700 mPa.s. By the additive of the inert solids, which for itself alone not when defoamers are effective, surprisingly the effectiveness of the oil in water emulsions becomes lowered practically not as defoamers. The particle size of the inert,

water-insoluble solids always lies below the particle size of the oil phase of the oil in water emulsion and amounts to at the most 95% of the particle size of the oil in water emulsion used in each case.

The inventive oil in water emulsions become used as defoamers in foam-formed aqueous systems in such a quantity that on 100 Gew. - Parts of foam-formed Mediums for instance O, CO₂ to O, 5, preferably O, O5 to O, 3 Gew. - Parts of the antifoaming agent emulsion come. The inventive antifoaming agent emulsions are used in particular as defoamers with the production of paper, whereby they become both during the sulfite cellulose cooking and used with the papermaking, the stuff and in paper caper colors. The defoamers can be used also in food industry, the strength industry as well as in purification plants with the foam control.

The parts indicated in the examples are parts by weight, the percentage figures relate itself on the weight of the fabrics. Die mittlere Teilchengrösse der in Wasser emulgierten Teilchen der Ölphase wurde mit Hilfe eines Coulter-Counters bestimmt, der Teilchendurchmesser der inerten Feststoffe war 0,5 bis 15 µm.

Determination of the foam value:

In a trough from a transparent plastic 5 l of a foam-developing stuff suspension is umgepumpt in each case 5 minutes. The foam quantity formed at the surface of the Stoff suspension becomes then with the help of a grid at the wall of the duct in unit areas (cm²) measured and as so-called foam value to the judgment of the effectiveness of a defoamer indicated.

Pumpt man die Papierstoffsuspension in Abwesenheit eines Entschäumers um, so beträgt der Schaumwert nach 5 Minuten 1 200 cm². By the addition of in each case 2 mg/l an effective defoamer to the stuff suspension this value significant is reduced, so that it represents a dimension for the effectiveness of a defoamer. One sets however in place of a defoamer 2 mg/l a hydrophobisierten, inert, finely divided (O, 5 to 15 µm) solid, e.g. Kaolin, CaSO₄, Talkum, Kreide, Bariumsulfat, vernetzte Stärke, TiO₂, Bentonit, Al₂O₃ oder SiO₂ zu, so ändert sich der Schaumwert nicht.

Example 1

20, 5 parts of a mixture from Glycerintriestern from C16 to C18-Fettsäuren, a fat alcohol mixture of C16 to C20-Alkoholen and mineral oil in the weight ratio 14: 10: 6 becomes with 10 parts kaolin (middle particle diameter of more than 94% of the particles under 1 µm) with a temperature of 70 DEG C in an agitated container mixed. This mixture was then emulsified to a solution by 2 parts of an emulsifying agent (accumulation product of 25 mol ethylene oxide at 1 mol of Isooctylphenol, which are converted to the sulfuric acid half ester with sulphuric acid) in 67.5 portions waters. One appropriately submits the aqueous phase in a dispergator and fills those to kaolin contained oil phase too. One receives an oil in water emulsion, which with a temperature of 20 DEG C immediately after the production a viscosity of 450 mPa.s has and with the check of the Entschäumungswirkung a foam value of 191 cm² ergibt. The middle particle size of the oil phase amounts to 3 µm.

Comparison example 1

30, 5 parts of an oil phase from Glycerintriestern from C16 to C18-Fettsäuren, a fat alcohol mixture of C16 to C20-Alkoholen and mineral oil in the weight ratio of 14: 10: 6 in 69.5 parts of an aqueous phase of 67.5 parts water and 2 portions emulsifying agent (accumulation product of 25 mol ethylene oxide at 1 mol of Isooctylphenol, which are converted to the sulfuric acid half ester with sulphuric acid) are emulsified with a temperature of 70 DEG C in a dispergator. The middle particle size of the oil phase amounts to 3 µm. Bei der Prüfung der Wirksamkeit als Entschäumer wird ein Schaumwert von 189 cm² determined.

As this comparison example shows, the effectiveness of the defoamer becomes surprisingly practically not lowered in accordance with example 1 by the content of kaolin.

Example 2

15.5 parts of a mixture from Glycerintriestern from C16 to C18-Fettsäuren, a fat alcohol mixture of C16 to C20-Alkoholen and mineral oil in the weight ratio 14: 10: 6 is emulsified with 15 parts kaolin (middle particle size smaller 1 µm for 94% of the particles) with a temperature of 70 DEG C mixed and afterwards direct into 69.5 portions of a solution by 2 portions of the emulsifying agent in 67.5 portions waters, described in example 1. The middle particle diameter of the oil phase of the oil in waters - antifoaming agent emulsion amounts to 2.5 µm. With the check of the effectiveness of the emulsion as defoamers a foam value of 182 is cm² determined.

Example 3

25.5 parts of a mixture from Glycerintriestern from C16 to C18-Fettsäuren, a fat alcohol mixture of C16 to C20-Alkoholen and mineral oil in the weight ratio 14: 10: 6 becomes mixed on a temperature of 70 DEG C heated and with 5 parts of a finely divided chalk (middle particle diameter smaller 1 µm for 96% of the particles). This mixture is then emulsified into 69.5 parts of an aqueous solution, which contains 2 portions of the emulsifying agent described in example 1 in 67.5 parts water dissolved. One receives an oil in water emulsion with a middle particle size of the oil phase from 3,5 µm. With the check of the effectiveness as defoamers after the described above measuring method a foam value of 194 is cm² determined.

Example 4

15.5 parts of a mixture from Glycerintriestern from C16 to C18-Fettsäuren, Fettalkohlgemisch von C16 to C20-Alkoholen and mineral oil in the weight ratio 14: 10: 6 is intimately mixed on a temperature of 70 DEG C heated and with 15 parts chalk of a middle particle size of smaller 1 µm for 96% of the particles. This mixture is then emulsified directly in 69.5 parts of a solution by 2 parts of the emulsifying agent in 67.5 portions waters, described in example 1. One receives an oil in water emulsion, whose middle particle size of the oil phase amounts to 3.5 µm. With the check of the effectiveness of this emulsion as defoamers after the described above method a foam value of 187 is cm² obtained.

Example 5

15.5 parts of a mixture from Glycerintriestern from C16 to C18-Fettsäuren, Fettalkohlgemisch von C16 to C20-Alkoholen and

mineral oil in the weight ratio 14: 10: 6 is intimately mixed on a temperature of 70 DEG C heated and with 15 parts calcium sulfate of a middle particle size of 0, 2 μ m. This mixture is then in-emulsified into 69.5 portions of an aqueous solution, which contains 2 parts of the emulsifying agent dissolved described in example 1. It results an oil in water emulsion, whose middle particle size of the oil phase 3 amounts to μ m and which cm< with the check as defoamer after the indicated above method a foam value of 196; 2> results in.

Example 6

15.5 parts of a mixture from Glycerintriesters from C16 to C18-Fettsäuren, Alkohlgemisch von C16 to C18-Alkoholen and mineral oil in the weight ratio 14: 10: 6 is intimately mixed on a temperature of 80 DEG C heated and with 15 parts talcum powder of a middle particle size of 0, 5 μ m. This mixture is then emulsified in 69.5 parts of an aqueous solution, which contains 2 parts of the emulsifying agent dissolved described in example 1. It results an oil in water emulsion, whose oil phase has a middle particle size of 3 μ m, and which cm< with the check as defoamer after the described above method a foam value of 186; 2> results in.

Example 7

15.5 parts of a mixture from Glycerin triester of C16-C18-Fettsäuren, a fat alcohol mixture of C16-C20-Alkoholen and mineral oil in the weight ratio 14: 10: 6 is mixed on a temperature of 70 DEG C heated and with 15 parts of a mikrokristallinen cellulose, whose middle particle size is appropriate below 1 μ m, intimately. This mixture is then emulsified in 69.5 parts of an aqueous solution, which contains 2 parts of the emulsifying agent described in example 1. Results an oil in water emulsion, whose oil phase has a particle size of 4 μ m, and which cm< with the check of the effectiveness as defoamer after the described above method a foam value of 200; 2> results in.

Example 8

15.5 parts of a mixture from Glycerintriesters of C16-C18-Fettsäuren, a fat alcohol mixture of C16-C20-Alkoholen and mineral oil in the weight ratio of 14: 10: 6 becomes homogenized on a temperature of 80 DEG C heated and with 15 parts of a commercial crosslinked thickness, whose middle particle size is appropriate below 5 μ m. In such a way the resultant mixture then into 69.5 parts of an aqueous solution one emulsifies, the 2 Gew. - Parts of the emulsifying agent dissolved described in example 1 contains. One receives an oil in water emulsion with a particle size of the oil phase from 8 μ m. With the check of the effectiveness as defoamers for this emulsion a foam value of 179 is cm< 2> determined.

Example 9

To 100 parts of an emulsion from 30 parts of a mixture from Glycerintriesters of C16-C18-Fettsäuren, a fat alcohol mixture of C16-C20-Alkoholen and mineral oil in the weight ratio by 14:1 0: 6 in 70 parts water, which contains 2 parts by weight of the emulsifying agent dissolved described in the example 1, 3 parts kaolin with a temperature of 30 DEG C (particle diameter become < 1 μ m for 94% of the particles) given and in a dispergator thereby homogenized. The particle size of the oil phase of the so obtained emulsion amounts to 6 μ m. The emulsion results in a foam value of 184 in the case of the above-described check cm< 2>.

Example 10

Example 9 is repeated with the exception that one adds parts Koalin of the indicated specification in place of 3 now 12. One receives an antifoaming agent emulsion, whose oil phase has a particle size of 6 μ m, and which cm< with the check in accordance with the indicated above regulation a foam value of 186; 2> results in.